[16] B. M. Gimarc, D. S. Warren, *Inorg. Chem.* **1993**, *32*, 1850–1856; M. W. Schmidt, M. S. Gordon, *Inorg. Chem.* **1985**, *24*, 4503–4506; R. H. Ahlrichs, S. Brode, C. Ehrhardt, *J. Am. Chem. Soc.* **1985**, *107*, 7260–7264; G. Trinquier, J.-P. Daudey, N. Komiha, *J. Am. Chem. Soc.* **1985**, *107*, 7210–7212.
[17] G. M. Sheldrick, SHELXS-97, University Göttingen, **1997**.
[18] W. Herrendorf, H. Bärnighausen, HABITUS, Universities Karlsruhe and Gießen, **1993**.
[19] G. M. Sheldrick, SHELXL-97, University Göttingen, **1997**.

Hybrid Molecular Materials Based on Covalently Linked Inorganic Polyoxometalates and Organic Conjugated Systems**

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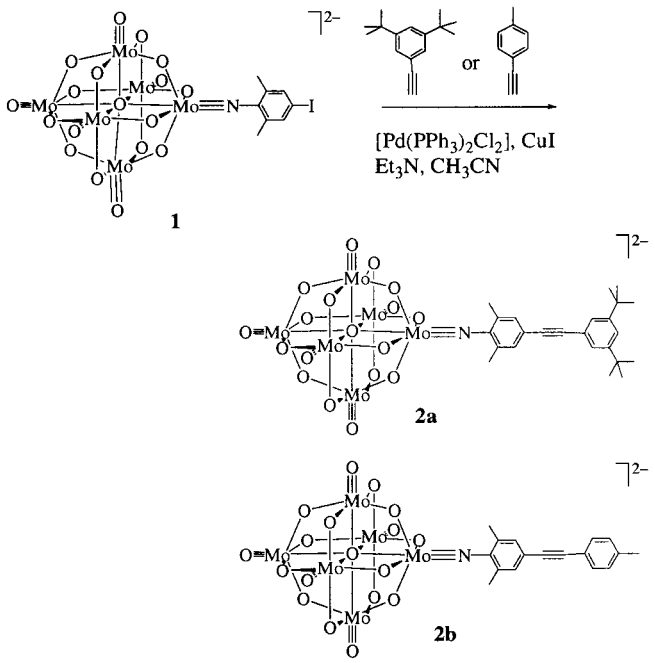
Polyoxometalate (POM) chemistry has advanced dramatically during the past two decades, and numerous new structural types with fascinating topological beauty and important electronic, optical, and catalytic properties have been developed.[1–4] Parallel to the rapid progress made on these inorganic metal–oxygen cluster anions, studies on organic and polymeric conjugated materials have also exploded and flourished.[5–8] The fact that the Nobel Prize in chemistry for 2000 went to three preeminent scientists working on conjugated polymers is the ultimate testimony to the important developments in organic conjugated systems.[9]

Although they are vastly different in molecular structures, POMs and organic conjugated molecules/polymers are both electrically active materials with similar electrical and optical properties such as photochromism, electrochromism, and conductivity. The underlying mechanisms of these properties are, however, different for the two types of materials, with dπ electrons responsible for the inorganic clusters, and delocalized π electrons responsible for the organic counterpart. While both areas have been enjoying considerable success, there has been little success in bringing these two types of materials together through covalent bonds.[10, 11] Not only will such hybrid materials combine the advantages of organic materials, such as ease in processing and structural fine tuning, with those of inorganic clusters, but the close interaction of organic delocalized π electrons with the cluster d electrons may bring exciting synergistic effects. Such materials with their unique structures are extremely interesting not only to synthetic chemists and materials scientists, but also to theoretical and experimental physicists.

Herein, we report the synthesis of such hybrid materials through Pd-catalyzed coupling reactions and demonstrate, for the first time, that iodo-functionalized hexamolybdates can undergo Pd-catalyzed coupling reactions with ethynylarenes. These reactions open an exciting research arena where a variety of hybrid materials containing covalently bonded POM clusters and organic conjugated segments can be prepared in a controllable and rational way.

Scheme 1 shows the structures and synthesis of the hybrid materials. Compound $[Bu_4N]_2$-**1** was synthesized by using an approach developed in our laboratory.[12] The coupling of



Scheme 1. Pd-catalyzed coupling of the iodo-funtionalized hexamolybdate anion **1** with alkynes.

$[Bu_4N]_2$-**1** with 1-ethynyl-3,5-di(*tert*-butyl)benzene or 1-ethynyl-4-methylbenzene was carried out in acetonitrile at room temperature under the protection of nitrogen.[13] The reaction is unusually fast and is completed in a few minutes as monitored by thin-layer chromatography. The cluster not only survived under the reaction conditions, it apparently activates the coupling reaction. The enhanced reactivity of the iodo function in **1** is presumably due to the electron-withdrawing nature of the Mo–N triple bond. Prolonged reaction time is found to be detrimental, as the coupling product slowly decomposes to its parent $\{Mo_6O_{19}\}$ cluster under the reaction conditions. Nevertheless, pure products $[Bu_4N]_2$-**2a** and $[Bu_4N]_2$-**2b** can be synthesized in excellent yields.

Both $[Bu_4N]_2$-**2a** and $[Bu_4N]_2$-**2b** exhibit excellent solubility in common organic solvents such as dichloromthane, chloroform, acetone, acetonitrile, THF, and DMF. They also show remarkable stability against O_2 and moisture. No obvious

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decomposition is observed after their solutions stand in air for nearly one month. The structures of the products were confirmed by elemental analysis, spectroscopic measurements, and X-ray single-crystal structure analysis. Figure 1 shows the ^{1}H NMR spectra of $[Bu_4N]_2$-**1**, $[Bu_4N]_2$-**2a**, and $[Bu_4N]_2$-**2b** in [D_6]acetone. All spectra show clearly resolved signals, all of which can be unambiguously assigned. In each case the integration matches well with the desired structure.

Single crystals of $[Bu_4N]_2$-**2b** were grown by diffusion of diethyl ether into a solution of the compound in acetonitrile. The crystals are very thin plates which generate rather weak X-ray diffraction signals. Nevertheless, the X-ray diffraction measurement does confirm the targeted structure.[14] Figure 2 shows the ORTEP drawing of the crystal structure of the anion **2b**. Compound $[Bu_4N]_2$-**2b** crystallizes in space group *C*2/*c* with two crystallographically independent anions in the asymmetric unit. One axis is significantly longer (ca. 60 Å) than the other two (22 and 19 Å). Similar to its precursor **1** and other arylimido derivatives of hexamolybdates, the Mo–N bond in **2b** shows triple-bond character, as evidenced by the short bond length (1.74 Å) and nearly linear Mo-N-C angle (171.4°). It is rather unusual that the oligo(phenylene acetylene) unit is not linear, instead showing some curvature.

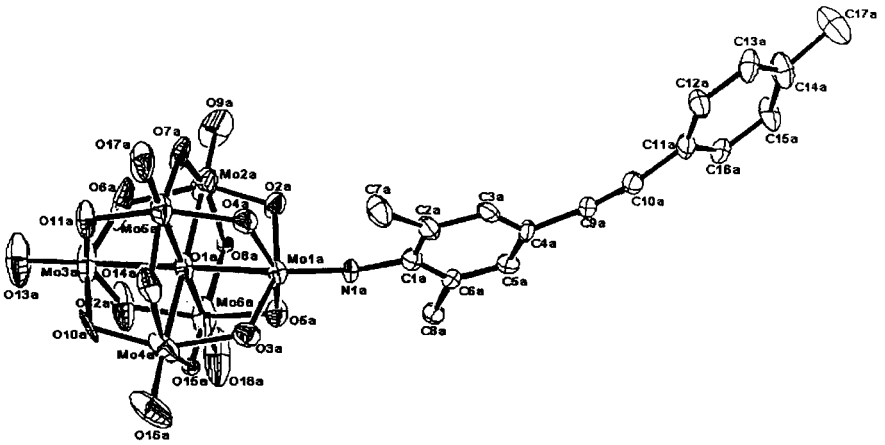

Figure 2. Structure of one of the two crystallographically independent anions of **2b** (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Mo1a-N1a 1.739(19), Mo2a-O9a 1.67(2), Mo3a-O13a 1.68(2), Mo4a-O16a 1.71(3), Mo5a-O17a 1.74(2), Mo6a-O18a 1.69(3), O1a-Mo1a 2.193(14), O1a-Mo6a 2.293(16), O1a-Mo5a 2.317(16), O1a-Mo4a 2.335(18), O1a-Mo3a 2.334(14), O1a-Mo2a 2.367(18), N1a-C1a 1.41(3), C1a-C6a 1.36(3), C1a-C2a 1.43(3), C2a-C3a 1.41(3), C2a-C7a 1.56(4), C3a-C4a 1.37(3), C4a-C5a 1.38(3), C4a-C9a 1.48(3), C5a-C6a 1.35(3), C6a-C8a 1.52(3), C9a-C10a 1.17(3), C10a-C11a 1.44(3), C11a-C16a 1.39(3), C11a-C12a 1.41(3), C12a-C13a 1.37(3), C13a-C14a 1.41(3), C14a-C15a 1.36(3), C14a-C17a 1.55(4), C15a-C16a 1.39(3), C1a-N1a-Mo1a 171.4(18), C10a-C9a-C4a 172(3), C9a-C10a-C11a 173(3).

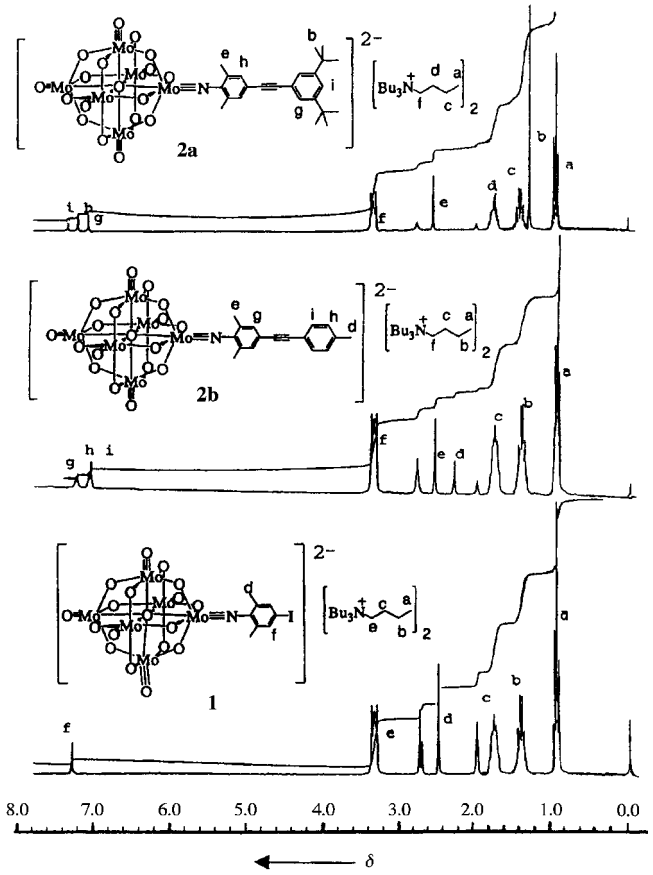

Figure 1. ^{1}H NMR spectra of $[Bu_4N]_2$-**1**, $[Bu_4N]_2$-**2a**, and $[Bu_4N]_2$-**2b** in [D_6]acetone. The two unlabeled peaks are solvent signals (acetone and water).

The electronic properties of functionalized hexamolybdates were studied by UV/Vis absorption and static fluorescence measurements. As shown in Figure 3, the lowest energy electronic absorptions are significantly red-shifted from parent $[Mo_6O_{19}]^{2-}$ to mono-arylimido hexamolybdate **1**, and to the coupling product **2a**. If, as commonly believed, the lowest energy absorption is due to the charge-transfer transition originated in a state dominated by Mo–N π-bonding,[15] the bathochromic shifts observed may imply that the Mo–N π bond is delocalized with the organic conjugated π electrons. In other words, there is a strong electronic interaction between the metal–oxygen cluster and the organic segment. Fluorescence studies show that **2a** and **2b** show no fluorescence under excitation from 200 nm to 500 nm. Considering the fact that oligo(phenylene ethynylene)s are highly fluorescent molecules,[16] the hexamolybdate

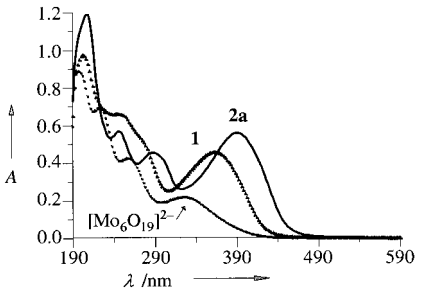

Figure 3. UV/Vis absorption spectra of $[Mo_6O_{19}]^{2-}$, **1**, and **2a**.

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cluster evidently acts as a fluorescence quencher, presumably by accepting the excited electrons.

In conclusion, the reported Pd-catalyzed C–C coupling of iodo-functionalized hexamolybdate building blocks and alkynes thus offers a route to hybrid materials in which POM clusters are covalently bonded with organic conjugated segments.

Experimental Section

A mixture containing $[Bu_4N]_2[Mo_6O_{18}{\equiv}NC_6H_2(CH_3)_2I]$ ($[Bu_4N]_2$-**1**), (2.00 g, 1.26 mmol), 1-ethynyl-3,5-di(*tert*-butyl)benzene or 1-ethynyl-4-methylbenzene (1.90 mmol, 1.5 equiv), $[Pd(PPh_3)_2Cl_2]$ (0.026 g, 0.03 equiv), CuI (0.014 g, 0.06 equiv), and triethylamine (1 g) was stirred in acetonitrile (40 mL) at room temperature for 20 min, which led to a shiny red solution. Dichloromethane (100 mL) was then added. The resulting solution was washed twice with H_2O and brine water, and then concentrated to about 10 mL. After the addition of hexane (200 mL) to the above concentrated solution, it was left standing for 2 h. The top yellowish clear solution was discarded. The oily dark red residue was dried under vacuum to yield the products as dark red solids ($[Bu_4N]_2$-**2a**, 85% yield; $[Bu_4N]_2$-**2b**, 72% yield).

$[Bu_4N]_2$-**2a**: Elemental analysis (%) for $C_{56}H_{101}N_3O_{18}Mo_6$: calcd: C 40.04, H 6.06, N 2.51; found: C 40.99, H 6.07, N 2.55; ^{1}H NMR (250 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 0.97$ (t, $J = 7.25$ Hz, 24H; CH_3), 1.34 (s, 18H; $C(CH_3)_3$), 1.47 (sextet, $J = 7.30$ Hz, 16H; CH_2), 1.83 (quintet, $J = 7.94$ Hz, 16H; CH_2), 2.64 (s, 6H; ArH), 3.45 (t, $J = 8.50$ Hz, 16H; NCH_2), 7.25 (s, 2H; ArH), 7.39 (s, 2H; ArH), 7.52 (s, 2H; ArH).

$[Bu_4N]_2$-**2b**: Elemental analysis (%) for $C_{49}H_{87}N_3O_{18}Mo_6$: calcd: C 37.21, H 5.54, N 2.66; found: C 36.83, H 5.32, N 2.61; ^{1}H NMR (250 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 0.99$ (t, $J = 7.38$ Hz, 24H; CH_3), 1.46 (sextet, $J = 7.3$ Hz, 16H; CH_2), 1.83 (quintet, $J = 7.94$ Hz, 16H; CH_2), 2.37 (s, 3H; ArH), 2.64 (s, 6H; ArH), 3.47 (t, $J = 8.5$ Hz, 16H; NCH_2), 7.23 (s, 2H; ArH), 7.25 (d, $J = 8.5$ Hz, 2H; ArH), 7.42 (d, $J = 7.25$ Hz, 2H; ArH).

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[1] M. T. Pope, *Heteropoly and Isopoly Oxometalates*: Springer, New York, **1983**.
[2] M. T. Pope, A. Müller, *Angew Chem*. **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl*. **1991**, *30*, 34.
[3] *Polyoxometalates: From Planotic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer Academic, Dordrecht, The Netherlands, **1994**.
[4] C. L. Hill, guest editor, *Chem. Rev*. **1998**, *98*, 8.
[5] *Handbook of Organic Conductive Molecules and Polymers I–IV* (Ed.: H. S. Nalwa), Wiley, Chichester, **1997**.
[6] *Conjugated Polymers* (Eds.: J. L. Bredas, R. Silbey), Kluwer Academic, Dordrecht, The Netherlands, **1991**.
[7] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416; *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
[8] M. Pope, C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed., Oxford University Press, Oxford, **1999**.
[9] R. Dagani, *Chem. Eng. News* **2000**, *78*(42), 4. (The Nobel Lectures of the three prize winners will appear in issue 14 of *Angewandte Chemie International Edition*.)
[10] J. L. Stark, V. G. Young, Jr., E. A. Maatta, *Angew. Chem.* **1995**, *107*, 2751; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2547.
[11] J. L. Stark, A. L. Rheingold, E. A. Maatta, *J. Chem. Soc. Chem. Commun*. **1995**, 1165.
[12] Y. Wei, B. Xu, C. L. Barnes, Z. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083.
[13] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467.
[14] Crystal structure data for $[Bu_4N]_2$-**2b**: $C_{49}H_{87}N_3O_{18}Mo_6$, $M_r = 1581.89$, monoclinic, *C2/c*, $a = 59.61(2)$, $b = 22.139(7)$, $c = 19.315(7)$ Å, $\beta = 93.541(5)$, $V = 25442(15)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.652$ g cm^{-3}, $T = 173(2)$ K, crystal size $= 0.35 \times 0.25 \times 0.05$ mm, $\mu = 1.197$ mm^{-1}, $\lambda = 0.71073$ Å. A total of 56870 reflections (18191 independent, $R_{int} = 0.0899$) were collected on a Bruker SMART system ($2\theta_{max} = 46.50$). The structure was solved by direct methods (SHELXS, 1997) and refined by full-matrix least-squares (on F^2) and difference Fourier cycles (SHELXL, 1997). A semiempirical absorption correction (SADABS, G. M. Sheldrick, 1996) was applied ($T_{max} = 0.86$, $T_{min} = 0.62$). All non-hydrogen atoms were refined anisotropically and no attempts were done for H atoms. Final residuals ($I > 2\sigma(I) = 10777$) were $R_1 = 0.0933$, and $wR_2 = 0.2680$. Largest difference peak and hole $= 3.258$ and -2.752 e Å^{-3}. GOF (F^2) $= 1.046$. Drawings were generated using ORTEP-III (Burnett & Johnson, 1996). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154486. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[15] J. S. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta, *J. Am. Chem. Soc.* **2000**, 122, 639.
[16] R. Giesa, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1996**, *36*, 631.

Chemoenzymatic-Chemical Synthesis of a (2-3)-Sialyl T Threonine Building Block and Its Application to the Synthesis of the N-Terminal Sequence of Leukemia-Associated Leukosialin (CD 43)**

Nicole Bézay, Gregor Dudziak, Andreas Liese, and Horst Kunz*

Dedicated to Professor Dieter Hoppe on the occasion of his 60th birthday

Enzymatic reactions are valuable tools in syntheses of polyfunctional natural products and drugs. This holds true, in particular, for syntheses of oligosaccharides and their glycoconjugates, since numerous protecting-group manipulations can be avoided and glycosidic linkages can be formed regio- and stereoselectively by using glycosyltransferases[1] and glycosidases.[2] Successful enzymatic chain extensions of saccharides have been reported, in particular, for the formation of oligosaccharides and glycopeptides that contain sialic acid, in the course of which the enzymatic reactions constitute the final steps of the whole synthesis.[3] If, however, enzymatically prepared sialyl glycoconjugates are to be used in continuing chemical syntheses (e.g. of glycopeptides), their numerous functional groups must be blocked by selectively removable protecting groups.

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